Libxc: a library of exchange and correlation functionals for density functional theory

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The central quantity of density functional theory is the so-called exchange-correlation functional. This quantity encompasses all non-trivial many-body effects of the ground-state and has to be approximated in any practical application of the theory. For the past 50 years, hundreds of such approximations have appeared, with many successfully persisting in the electronic structure community and literature. Here, we present a library that contains routines to evaluate many of these functionals (around 180) and their derivatives.

I. INTRODUCTION

Density functional theory (DFT) is perhaps one of the most successful theories in Physics and in Chemistry of the last half-century [1–4]. It is currently used to predict the structure and the properties of atoms, molecules, and solids; it is a key ingredient of the new field of Materials Design, where one tries to create new materials with specific properties; it is making its way in Biology as an important tool in the investigation of proteins, DNA, etc. These are only a few examples of a discipline that even now, almost 50 years after its birth, is growing at an exponential rate.

Almost all applications of DFT are performed within the so-called Kohn-Sham scheme [5], that uses a non-interacting electronic system to calculate the density of the interacting system [6]. The Kohn-Sham scheme leeds to the following equations. (Hartree atomic units are used throughout the paper, i.e. $e^2 = \hbar = m_e = 1$.)

$$\left[-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{Hartree}}[n](\mathbf{r}) + v_{\text{xc}}[n](\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) , \qquad (1)$$

where the first term represents the kinetic energy of the electrons; the second is the external potential usually generated by a set of Coulombic point charges (sometimes described by pseudopotentials); the third term is the Hartree potential that describes the classical electrostatic repulsion between the electrons,

$$v_{\text{Hartree}}[n](\mathbf{r}) = \int d^3 r' \, \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} , \qquad (2)$$

and the exchange-correlation (xc) potential $v_{\text{xc}}[n]$ is defined by

$$v_{\text{xc}}[n](\mathbf{r}) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} . \qquad (3)$$

$E_{\text{xc}}[n]$ is the xc energy functional. Note that by $[n]$ we denote that the quantity is a *functional* of the electronic density,

$$n(\mathbf{r}) = \sum_i^{\text{occ.}} |\psi_i(\mathbf{r})|^2 , \qquad (4)$$

where the sum runs over the occupied states.

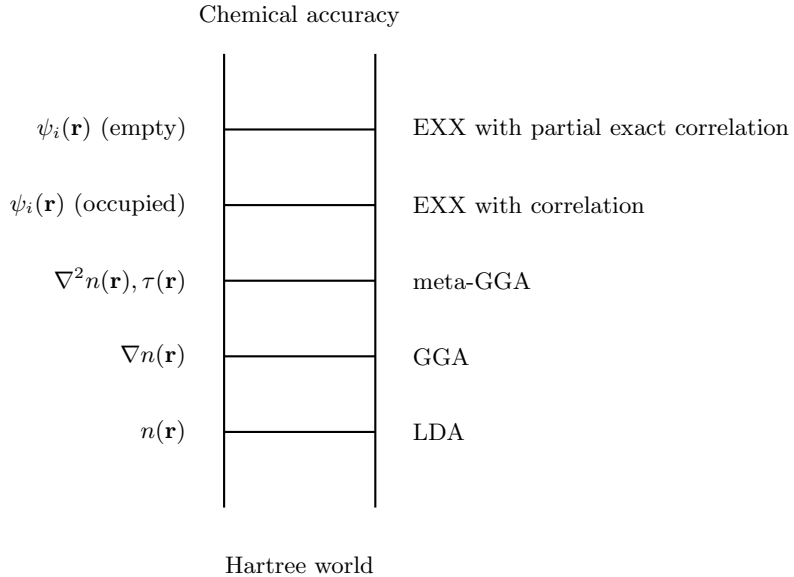*Corresponding author. Electronic address: marques@tddft.org

Chemical accuracy

$\psi_i(\mathbf{r})$ (empty) — EXX with partial exact correlation

$\psi_i(\mathbf{r})$ (occupied) — EXX with correlation

$\nabla^2 n(\mathbf{r}), \tau(\mathbf{r})$ — meta-GGA

$\nabla n(\mathbf{r})$ — GGA

$n(\mathbf{r})$ — LDA

Hartree world

FIG. 1: Jacob's ladder of density functional approximations for the xc energy.

The central quantity of this scheme is the xc energy $E_{\mathrm{xc}}[n]$ that describes all non-trivial many-body effects. Clearly, the exact form of this quantity is unknown and it must be approximated in any practical application of DFT. We emphasize that the precision of any DFT calculation depends solely on the form of this quantity, as this is the only real approximation in DFT (neglecting numerical approximations that are normally controllable).

The first approximation to the exchange energy, the local density approximation (LDA), was already proposed by Kohn and Sham in the same paper where they described their Kohn-Sham scheme [5]. It states that the value of xc energy density at any point in space is simply given by the xc energy density of a homogeneous electron gas (HEG) with electronic density $n(\mathbf{r})$. Mathematically, this is written as

$$E_{\mathrm{xc}}^{\mathrm{LDA}} = \int d^3 r \, n(\mathbf{r}) e_{\mathrm{xc}}^{\mathrm{HEG}}(n(\mathbf{r})) , \qquad (5)$$

where $e_{\mathrm{xc}}^{\mathrm{HEG}}(n)$ is the xc energy *per electron* of the HEG. Note that this quantity is a *function* of n. While the exchange contribution $e_{\mathrm{x}}^{\mathrm{HEG}}(n)$ can be easily calculated analytically, the correlation contribution is usually taken from Quantum Monte-Carlo simulations [7, 8]. As defined, the LDA is unique, but, as we will see in the A, even such precise definition can give rise to many different parameterizations.

During the past 50 years, hundreds of different forms appeared [9] and they are usually arranged in families, which have names such as generalized-gradient approximations (GGAs), meta-GGAs, hybrid functionals, etc. In 2001, John Perdew came up with a beautiful idea on how to illustrate these families and their relationship [10]. He ordered these families as rungs in a ladder that leads to the heaven of "chemical accuracy", and that he christened the Jacob's ladder of density functional approximations for the xc energy (see Fig. 1). Every rung adds a dependency on another quantity, thereby increasing the precision of the functional but also increasing the numerical complexity and the computational time.

At the bottom of the ladder we find the LDA, a functional that depends locally on the density only. The second rung is occupied by the GGA

$$E_{\mathrm{xc}}^{\mathrm{GGA}} = \int d^3 r \, n(\mathbf{r}) e_{\mathrm{xc}}^{\mathrm{GGA}}(n(\mathbf{r}), \nabla n(\mathbf{r})) . \qquad (6)$$

As one can see, one now adds the gradient of the density, a semi-local quantity that depends on an infinitesimal region around $\mathbf{r}$, as a parameter to the energy density. Note that there is a considerable amount of craftsmanship and physical/chemical intuition going into the creation of the function $e_{\mathrm{xc}}^{\mathrm{GGA}}(n, \nabla n)$, but also a fair quantity of arbitrariness. It is therefore not surprising that many different forms were proposed over the years. The same is true for the functionals on the next rung, the meta-GGAs

$$E_{\mathrm{xc}}^{\mathrm{mGGA}} = \int d^3 r \, n(\mathbf{r}) e_{\mathrm{xc}}^{\mathrm{mGGA}}(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau(\mathbf{r})) . \qquad (7)$$

This time one adds the Laplacian of the density $\nabla^2 n(\mathbf{r})$ and also (twice) the kinetic energy density

$$\tau(\mathbf{r}) = \sum_i^{\text{occ}} |\nabla \psi_i(\mathbf{r})|^2 \,. \tag{8}$$

Note that the meta-GGAs are effectively orbital functionals due to the dependence in $\tau(\mathbf{r})$.

The forth rung is occupied by functionals that include the exact-exchange (EXX) contribution to the energy

$$E_{\text{x}}^{\text{EXX}} = -\frac{1}{2} \int d^3 r \int d^3 r' \, \frac{\psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r}')\psi_j^*(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \,. \tag{9}$$

These functionals can include the whole $E_{\text{x}}^{\text{EXX}}$ or only a fraction of it, and $E_{\text{x}}^{\text{EXX}}$ can be evaluated with the bare Coulomb interaction or with a screened version of it. Furthermore, one can add a (semi-)local xc term or one that depends on the orbitals. In any case, the fourth rung only includes functionals that depend on the *occupied* orbitals only. Notorious examples of functionals on this rung are the hybrid functionals

$$E_{\text{xc}}^{\text{Hyb}} = a_x E_{\text{x}}^{\text{EXX}} + E_{\text{xc}}^{\text{mGGA}}[n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau(\mathbf{r})] \,. \tag{10}$$

Note that the local part of this functional can be a meta-GGA, a GGA, or even an LDA.

Finally, on the last rung of Jacob's ladder one finds functionals that depend on the empty (virtual) Kohn-Sham orbitals. Perhaps the best known example of these functionals is the random-phase approximation (RPA).

In a practical DFT calculation one needs typically to evaluate both E_{xc} and v_{xc}. Furthermore, to obtain response properties higher derivatives of E_{xc} are required. For example, in first order one can get the electric polarizability, the magnetic susceptibility, phonon frequencies, etc., and these usually require the knowledge of the xc kernel

$$f_{\text{xc}}(\mathbf{r}, \mathbf{r}') = \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \,. \tag{11}$$

In second order one can obtain, e.g., hyperpolarizabilities, Raman tensors, etc., but these calculations usually require

$$k_{\text{xc}}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') = \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}') \delta n(\mathbf{r}'')} \,. \tag{12}$$

The calculation of these derivatives is fairly straightforward by using basic functional analysis and the chain rule for functional derivatives. We give here as an example the case of the xc potential for a GGA

$$v_{\text{xc}}^{\text{GGA}}(\mathbf{r}) = e_{\text{xc}}^{\text{GGA}}(n(\mathbf{r}), \nabla n(\mathbf{r})) + \int d^3 r \, n(\mathbf{r}) \left. \frac{\partial e_{\text{xc}}^{\text{GGA}}}{\partial n} \right|_{\substack{n = n(\mathbf{r}) \\ \nabla n = \nabla n(\mathbf{r})}} \delta(\mathbf{r} - \mathbf{r}')$$

$$+ \int d^3 r \, n(\mathbf{r}) \left. \frac{\partial e_{\text{xc}}^{\text{GGA}}}{\partial \nabla n} \right|_{\substack{n = n(\mathbf{r}) \\ \nabla n = \nabla n(\mathbf{r})}} \nabla \delta(\mathbf{r} - \mathbf{r}') \,. \tag{13}$$

Integrating by parts the third term, one finally arrives at

$$v_{\text{xc}}^{\text{GGA}}(\mathbf{r}) = e_{\text{xc}}^{\text{GGA}}(n(\mathbf{r}), \nabla n(\mathbf{r})) + n(\mathbf{r}) \left. \frac{\partial e_{\text{xc}}^{\text{GGA}}}{\partial n} \right|_{\substack{n = n(\mathbf{r}) \\ \nabla n = \nabla n(\mathbf{r})}} - \nabla \left[n(\mathbf{r}) \left. \frac{\partial e_{\text{xc}}^{\text{GGA}}}{\partial \nabla n} \right|_{\substack{n = n(\mathbf{r}) \\ \nabla n = \nabla n(\mathbf{r})}} \right] \,. \tag{14}$$

Clearly, higher functional derivatives of E_{xc} involve higher partial derivatives of e_{xc}.

By now it is clear what a code needs to implement for the functionals of the first three rungs: given $n(\mathbf{r})$, and possibly $\nabla n(\mathbf{r})$, $\nabla^2 n(\mathbf{r})$, and $\tau(\mathbf{r})$, one needs the xc energy density $e_{\text{xc}}(\mathbf{r})$ and all relevant partial derivatives of this quantity. This is indeed the information that is provided by Libxc. For hybrid functionals the library also returns, besides the semi-local part, also the mixing coefficient a_x. Unfortunately, EXX and other functionals of the forth and fifth rang are too dependent on the actual numerical representation of the wave-functions and can not be easily included in a generic library.

Finally, we would like to mention that some applications of DFT do not use the Kohn-Sham scheme, but try to approximate the kinetic energy functional directly in terms of the density. This approach follows the path that was laid down in the 1927 by Thomas and Fermi [11, 12], and is sometimes referred to as "orbital-free DFT" [13]. In this case, we also need a functional form (either an LDA or a GGA) for the kinetic energy, and many of these are present in Libxc. A good review of functionals for the kinetic energy density can be found in Ref. [14].

Note that even if the discussion above was restricted to spin-compensated systems for the sake of simplicity, all functionals of Libxc can also be used with spin-polarization.

II. SOME HISTORY

LIBXC started as a spin-off project during the initial development of the (time-dependent) DFT code OCTOPUS [15–18]. At that point it became clear that the task of evaluation of the xc functional was completely independent of the main structure of OCTOPUS, and could therefore be transformed into a library. The first steps into the development of LIBXC were taken in September 2006, and the first usable version of the library included a few of the most popular LDA and GGA functionals.

At the same time, the European Theoretical Spectroscopy Facility was carrying a coordinate effort to improve code interoperability and re-usability of its software suite, so efforts were almost immediately made to interface those codes with LIBXC. This catalyzed the development of the library and accelerated its dissemination in the community.

During the following years, the library was expanded following two main lines:

(i) To include as many functionals as possible (by now we include around 180 — see A). This was done for several reasons. First, we implemented nearly all of the "old" functionals that played an important role in the development of DFT. From this perspective, we can look at LIBXC as a "living museum" of the history of this important discipline. It also allows users to reproduce old results with little effort. Secondly, many of the functionals that are proposed nowadays are implemented in LIBXC within weeks from the moment they are published. In this way new developments are very rapidly available in several different codes, allowing for these new functionals to be quickly tested and benchmarked. Note that we have an agnostic policy, i.e. we try to include the maximum possible number of functionals, without making any judgment of value concerning their beauty, elegance, or usefulness. This judgment is left for the final user to perform.

(ii) To include derivatives of the xc energy up to high orders. As we stated before, to perform a standard Kohn-Sham calculation one only requires the xc energy functional and its first derivatives. However, higher derivatives are essential in order to obtain response properties. Of course, these higher derivatives can be calculated numerically from lower-order derivatives, but this procedure tends to introduce unnecessary errors and instabilities in the calculations. We therefore implemented derivatives up to the third order for the LDAs and up to second order for the other functionals. We note that these derivatives are hand-coded, and not automatically generated from the output of symbolic manipulation software [19, 20]. Even if the latter approach is excellent in order to test implementations, the automatically generated code is often extremely verbose, inefficient, and unreadable. Note that LIBXC includes automatic procedures to check the implementation of the analytic derivatives.

At the beginning, LIBXC was used exclusively in the code OCTOPUS. However, since then several other codes from both the Solid-State Physics and Quantum Chemistry communities started to use this library. The list of codes that use LIBXC at the time of writing is as follows (in alphabetical order):

- ABINIT [21–23] (http://www.abinit.org/) — This is a general purpose plane-wave code. Besides the basic functionality, ABINIT also includes options to optimize the geometry, to perform molecular dynamics simulations, or to calculate dynamical matrices, Born effective charges, dielectric tensors, and many more properties.

- APE [24] (http://www.tddft.org/programs/APE) — The atomic pseudopotential engine (APE) is a tool for generating atomic pseudopotentials within DFT. It is distributed under the GPL and it produces pseudopotential files suitable for use with several codes.

- ATOMPAW [25] (http://www.wfu.edu/~natalie/papers/pwpaw/man.html) — The computer program ATOM-PAW generates projector and basis functions which are needed for performing electronic structure calculations based on the projector augmented wave (PAW) method. The program is applicable to materials throughout the periodic table.

- ATOMISTIX TOOLKIT [26, 27] (http://quantumwise.com) — This is a software package that uses non-equilibrium Green's functions simulations to study transport properties like I-V characteristics of nanoelectronic devices. It uses a powerful combination of DFT, semi-empirical tight-binding, and classical potentials.

- BIGDFT [28, 29] (http://inac.cea.fr/L_Sim/BigDFT/) — BIGDFT is a DFT massively parallel electronic structure code using a wavelet basis set. Wavelets form a real space basis set distributed on an adaptive mesh. Thanks to its Poisson solver based on a Green's function formalism, periodic systems, surfaces and isolated systems can be simulated with the proper boundary conditions.

- DP [30] (http://www.dp-code.org/) — Dielectric properties (DP) is a Linear Response TDDFT code, in frequency-reciprocal and frequency-real space, that uses a plane-wave basis set.

- ELK (http://elk.sourceforge.net/) — An all-electron full-potential linearized augmented-plane wave (FP-LAPW) code with many advanced features. This code is designed to be as simple as possible so that new

developments in the field of density functional theory (DFT) can be added quickly and reliably. The code is freely available under the GNU General Public License.

- ERKALE (http://erkale.googlecode.com) — ERKALE is a quantum chemistry program developed by J. Lehtola used to solve the electronic structure of atoms, molecules and molecular clusters. The main use of ERKALE is the computation of X-ray properties, such as ground-state electron momentum densities and Compton profiles, and core (X-ray absorption and X-ray Raman scattering) and valence electron excitation spectra of atoms and molecules.

- EXCITING [31, 32] (http://exciting-code.org/) — EXCITING is a full-potential all-electron DFT package based on the linearized augmented plane-wave (LAPW) method. It can be applied to all kinds of materials, irrespective of the atomic species involved, and also allows for the investigation of the atomic-core region.

- GPAW [33, 34] (https://wiki.fysik.dtu.dk/gpaw) — GPAW is a DFT Python code based on the projector-augmented wave (PAW) method and the atomic simulation environment (ASE). It uses real-space uniform grids and multigrid methods or atom-centered basis-functions.

- HIPPO [35–37] — This is an electronic structure code, developed by N. Lathiotakis, that implements Reduced Density Matrix Functionals for atomic and molecular systems using Gaussian-type orbitals .

- OCTOPUS [15–18] (http://www.tddft.org/programs/octopus/) — OCTOPUS is a scientific program aimed at the *ab initio* virtual experimentation on a hopefully ever-increasing range of system types. Electrons are described quantum-mechanically within density-functional theory (DFT), and in its time-dependent form (TDDFT) when doing simulations in time. Nuclei are described classically as point particles. Electron-nucleus interaction is described within the pseudopotential approximation.

- YAMBO [38] (http://www.yambo-code.org/) — YAMBO is a Fortran/C code for many-body calculations in solid state and molecular physics. The code was originally developed in the Condensed Matter Theoretical Group of the Physics Department at the University of Rome "Tor Vergata" by A. Marini. Previous to its release under the GPL license, YAMBO was known as SELF.

This diversity of codes is extremely important, because in this way a certain functional can be tested and used with a variety of methods in different physical situations. For example, a meta-GGA developed within a certain code to get good band-gaps of solids can be immediately used in a different code (often after a simple recompilation) to obtain the ionization potential of molecules.

LIBXC is freely available from http://www.tddft.org/programs/Libxc, and it is distributed under the GNU Lesser General Public License v3.0. This license not only allows everyone to read, modify, and distribute the code, but also allows LIBXC to be linked from close-source codes. The reader is also referred to the web site to obtain more information, updated documentation, examples, new versions, etc.

As most open source projects, we strongly encourage contributions from researchers willing to contribute with the implementation of new functionals, higher derivatives, bug corrections, or even bug reports.

III.   AN EXAMPLE

A.   Calling LIBXC

Probably the best way to explain the usage of LIBXC is through an example. The following small program calculates the xc energy for a given functional for several values of the density; the available C bindings can be found in header file `xc.h`. More information and examples can be found in the manual and in the header files.

```
#include <stdio.h>
#include <xc.h>

int main()
{
  xc_func_type func;
  double rho[5] = {0.1, 0.2, 0.3, 0.4, 0.5};
  double sigma[5] = {0.2, 0.3, 0.4, 0.5, 0.6};
  double ek[5];
```

```
      int i, func_id = 1;

      /* initialize the functional */
      if(xc_func_init(&func, func_id, XC_UNPOLARIZED) != 0) {
        fprintf(stderr, "Functional '%d' not found\n", func_id);
        return 1;
      }

      /* evaluate the functional */
      switch(func.info->family)
        {
        case XC_FAMILY_LDA:
          xc_lda_exc(&func, 5, rho, ek);
          break;
        case XC_FAMILY_GGA:
        case XC_FAMILY_HYB_GGA:
          xc_gga_exc(&func, 5, rho, sigma, ek);
          break;
        }

      for(i=0; i<5; i++) {
        printf("%lf %lf\n", rho[i], ek[i]);
      }

      /* free the functional */
      xc_func_end(&func);
    }
```

The functionals are divided in families (LDA, GGA, etc.). Given a functional identifier, `func_id`, the functional is initialized by `xc_func_init`, and evaluated by `xc_XXX_exc`, which returns the energy per unit volume (`ek`). Finally, the function `xc_func_end` cleans up. We note that we follow the convention used in Quantum Chemistry and, instead of passing the full gradient of the density, we use the variable

$$\sigma(\mathbf{r}) = \nabla n(\mathbf{r}) \cdot \nabla n(\mathbf{r}) \, . \tag{15}$$

Converting between partial derivatives with respect to σ and ∇n is trivially done with the use of the chain rule. All the quantities passed to and returned by the library are in atomic units.

Fortran 90 bindings are also included in LIBXC. These can be found in the file `libxc_master.F90`. In general, calling LIBXC from Fortran is as simple as from C. Here is the previous example in Fortran:

```
program lxctest
   use xc_f90_types_m
   use xc_f90_lib_m

   implicit none

   TYPE(xc_f90_pointer_t) :: xc_func
   TYPE(xc_f90_pointer_t) :: xc_info
   real(8) :: rho(5) = (/0.1, 0.2, 0.3, 0.4, 0.5/)
   real(8) :: sigma(5) = (/0.2, 0.3, 0.4, 0.5, 0.6/)
   real(8) :: ek(5)
   integer :: i, func_id

   func_id = 1

   ! initialize the functional
   call xc_f90_func_init(xc_func, xc_info, func_id, XC_UNPOLARIZED)

   ! evaluate the functional
```

```
  select case (xc_f90_info_family(xc_info))
  case(XC_FAMILY_LDA)
    call xc_f90_lda_exc(xc_func, 5, rho(1), ek(1))
  case(XC_FAMILY_GGA, XC_FAMILY_HYB_GGA)
    call xc_f90_gga_exc(xc_func, 5, rho(1), sigma(1), ek(1))
  end select

  do i = 1, 5
    write(*,"(F8.6,1X,F9.6)") rho(i), ek(i)
  end do

  ! free the functional
  call xc_f90_func_end(xc_func)

end program lxctest
```

B. The info structure

Besides the mathematical formulas necessary to evaluate the functional and its derivatives, LIBXC includes a considerable amount of metadata that is quite useful for both the calling program and for the end user. This information is contained for each functional in the structure xc_func_info_type. The relevant part of this structure for the end user is defined as

```
/* flags that can be used in info.flags */
#define XC_FLAGS_HAVE_EXC       (1 <<  0) /*    1 */
#define XC_FLAGS_HAVE_VXC       (1 <<  1) /*    2 */
#define XC_FLAGS_HAVE_FXC       (1 <<  2) /*    4 */
#define XC_FLAGS_HAVE_KXC       (1 <<  3) /*    8 */
#define XC_FLAGS_HAVE_LXC       (1 <<  4) /*   16 */
#define XC_FLAGS_1D             (1 <<  5) /*   32 */
#define XC_FLAGS_2D             (1 <<  6) /*   64 */
#define XC_FLAGS_3D             (1 <<  7) /*  128 */
#define XC_FLAGS_STABLE         (1 <<  9) /*  512 */
#define XC_FLAGS_DEVELOPMENT    (1 << 10) /* 1024 */

typedef struct{
  int   number;   /* indentifier number */
  int   kind;     /* XC_EXCHANGE and/or XC_CORRELATION */

  char *name;     /* name of the functional, e.g. "PBE" */
  int   family;   /* type of the functional, e.g. XC_FAMILY_GGA */
  char *refs;     /* references                              */

  int   flags;    /* see above for a list of possible flags */

  ...
} xc_func_info_type;
```

For example, for the Slater exchange functional, this structure is defined as

```
const XC(func_info_type) XC(func_info_lda_x) = {
  XC_LDA_X,
  XC_EXCHANGE,
  "Slater exchange",
  XC_FAMILY_LDA,
  "PAM Dirac, Proceedings of the
   Cambridge Philosophical Society 26, 376 (1930)\n"
  "F Bloch, Zeitschrift fuer Physik 57, 545 (1929)",
```

```
XC_FLAGS_3D | XC_FLAGS_HAVE_EXC | XC_FLAGS_HAVE_VXC | XC_FLAGS_HAVE_FXC
            | XC_FLAGS_HAVE_KXC,

  ...
};
```

Note that the references are separated by a newline. The user of the library can access the information in the following way:

```
#include <stdio.h>
#include <xc.h>

int main()
{
  xc_func_type func;
  xc_func_init(&func, XC_GGA_X_B88, XC_UNPOLARIZED);
  printf("The functional '%s' is defined in the reference(s):\n%s\n",
    func.info->name, func.info->refs);
  xc_func_end(&func);
}
```

IV.   CONCLUSIONS AND THE FUTURE

Libxc is by now seven years old, and the code is quite stable and in use by hundreds of scientists around the world. We are committed to continue the development of the library in the future, mainly by following the two lines mentioned before: include all functionals, and their derivatives of the highest possible order. By now essentially all LDA and GGA functionals ever proposed in the literature are already included in the library. Unfortunately, important gaps still remain especially in the meta-GGAs and hybrid functionals. We will fill in those gaps in the near future. It is not clear if Libxc will ever include *all* functionals ever developed (especially, as several new functionals come out every year), but we will of course try...

V.   ACKNOWLEDGEMENTS

Appendix A: Available functionals

For convenience, functionals in Libxc are divided in exchange, correlation, and exchange-correlation functionals. This division is sometimes arbitrary, but it is often useful for the end user (who may fancy strange mixtures of functionals) and for the code developers.

Below we give a complete list of the functionals the library currently knows about. We note that many of these were tested against reference implementations, when available, or against published results. The functionals have a label that is used to identify the functional inside Libxc. Furthermore, the third column indicates the time in seconds required for 50,000,000 evaluations of the (spin-unpolarized) xc potential in a single core of an Intel Core 2 processor running at 2.83 GHz. As one can see, the typical execution time within Libxc is much smaller than the total time required in the whole calculation.

TABLE I: Functionals available in Libxc.

LDA Functionals

LDA Exchange

XC_LDA_X	LDA exchange	6.92	[40, 41]
XC_LDA_X_2D	Slater exchange in 2D	9.36	
XC_LDA_X_1D	Slater exchange in 1D	3382	[42]

LDA Correlation

XC_LDA_C_WIGNER	Wigner parametrization	6.55	[43]
XC_LDA_C_RPA	Random Phase Approximation	11.96	[44]
XC_LDA_C_HL	Hedin & Lundqvist	9.86	[45]
XC_LDA_C_GL	Gunnarsson & Lundqvist	12.19	[46]
XC_LDA_C_XALPHA	Slater's Xα (X-alpha)	9.33	
XC_LDA_C_VWN	Vosko, Wilk, & Nussair	24.14	[47]
XC_LDA_C_VWN_RPA	Vosko, Wilk, & Nussair (RPA)	18.21	[47]
XC_LDA_C_PZ	Perdew & Zunger	8.90	[48]
XC_LDA_C_OB_PZ	Ortiz & Ballone (PZ parametrization)	12.08	[8, 48, 49]
XC_LDA_C_PW	Perdew & Wang	17.63	[50]
XC_LDA_C_PW_RPA	Perdew & Wang fit to the RPA energy	28.16	[50]
XC_LDA_C_OB_PW	Ortiz & Ballone (PW parametrization)	12.43	[8, 49, 50]
XC_LDA_C_2D_AMGB	Attaccalite, Moroni, Gori-Giorgi, and Bachelet (LDA for 2D systems)	10.44	[51]
XC_LDA_C_2D_PRM	Pittalis, Räsänen, and Marques (LDA for 2D systems)	11.35	[52]
XC_LDA_C_vBH	von Barth & Hedin	10.40	[53]
XC_LDA_C_1D_CSC	Casula, Sorella & Senatore (LDA correlation for 1D systems)	28.85	[54]
XC_LDA_C_ML1	Modified LDA (version 1) of Proynov and Salahub	37.02	[55]
XC_LDA_C_ML2	Modified LDA (version 2) of Proynov and Salahub	51.99	[55]
XC_LDA_C_GOMBAS	Gombas	10.81	[56]

LDA Exchange-Correlation

XC_LDA_XC_TETER93	Teter 1993	9.22	[57]

LDA Kinetic Energy

XC_LDA_K_TF	Thomas-Fermi kinetic energy	6.74	[11, 12]
XC_LDA_K_LP	Lee and Parr Gaussian ansatz for the kinetic energy	7.99	[58]

GGA Functionals

GGA Exchange

XC_GGA_X_PBE	Perdew, Burke & Ernzerhof exchange	13.61	[59, 60]
XC_GGA_X_PBE_R	Perdew, Burke & Ernzerhof exchange (revised)	19.27	[61]
XC_GGA_X_MPBE	Adamo & Barone modification to PBE	19.39	[62]
XC_GGA_X_XPBE	Extended PBE by Xu & Goddard III	18.90	[63]
XC_GGA_X_B86	Becke 86 Xalfa,beta,gamma	18.64	[64, 65]
XC_GGA_X_B86_MGC	Becke 86 Xalfa,beta,gamma (with mod. grad. correction)	24.86	[64, 66]
XC_GGA_X_B88	Becke 88	20.97	[67]
XC_GGA_X_G96	Gill 96	15.57	[68]
XC_GGA_X_PW86	Perdew & Wang 86	32.31	[69]
XC_GGA_X_PW91	Perdew & Wang 91	48.02	[70]
XC_GGA_X_OPTX	Handy & Cohen OPTX 01	18.21	[71]
XC_GGA_X_DK87_R1	dePristo & Kress 87 (version R1)	19.10	[72]
XC_GGA_X_DK87_R2	dePristo & Kress 87 (version R2)	24.11	[72]
XC_GGA_X_LG93	Lacks & Gordon 93	32.74	[73]
XC_GGA_X_FT97_A	Filatov & Thiel 97 (version A)	22.05	[74]
XC_GGA_X_FT97_B	Filatov & Thiel 97 (version B)	26.86	[74]
XC_GGA_X_PBE_SOL	Perdew, Burke & Ernzerhof exchange (for solids)	19.33	[75]
XC_GGA_X_RPBE	Hammer, Hansen & Norskov (PBE-like)	17.14	[76]
XC_GGA_X_WC	Wu & Cohen	17.91	[77]

XC_GGA_X_AM05	Armiento & Mattsson 05 exchange	61.38 [78, 79]
XC_GGA_X_PBEA	Madsen 07	30.98 [80]
XC_GGA_X_mPW91	mPW91 of Adamo & Barone	47.19 [81]
XC_GGA_X_2D_B86_MGC	Becke 86 with modified gradient correction for 2D	13.49 [82]
XC_GGA_X_BAYESIAN	Bayesian best fit for the enhancement factor	18.91 [83]
XC_GGA_X_PBE_JSJR	Reparametrized PBE by Pedroza, Silva & Capelle	18.71 [84]
XC_GGA_X_OPTB88_VDW	opt-Becke 88 for vdW	25.24 [85]
XC_GGA_X_PBEK1_VDW	Reparametrized PBE for vdW	18.72 [85]
XC_GGA_X_OPTPBE_VDW	Reparametrized PBE for vdW	40.62 [85]
XC_GGA_X_RGE2	Regularized PBE	14.65 [86]
XC_GGA_X_RPW86	Refitted Perdew & Wang 86	30.61 [87]
XC_GGA_X_KT1	Keal and Tozer, version 1	23.96 [88]
XC_GGA_X_HERMAN	Herman Xalphabeta GGA	17.44 [89, 90]
XC_GGA_X_LBM	van Leeuwen & Baerends modified	30.98 [91]
XC_GGA_X_OL2	Exchange form based on Ou-Yang and Levy v.2	15.69 [92, 93]
XC_GGA_X_MB88	Modified Becke 88 for proton transfer	24.86 [94]
XC_GGA_X_APBE	mu fixed from the semiclassical neutral atom	18.71 [95]
XC_GGA_X_HTBS	Haas, Tran, Blaha, and Schwarz	26.17 [96]
XC_GGA_X_AIRY	Constantin et al based on the Airy gas	47.48 [97]
XC_GGA_X_LAG	Local Airy Gas	49.75 [98]
XC_GGA_X_SOGGA11	Second-order generalized gradient approximation 2011	20.40 [99]
XC_GGA_X_C09X	C09x to be used with the VdW of Rutgers-Chalmers	19.86 [100]

GGA Correlation

XC_GGA_C_PBE	Perdew, Burke & Ernzerhof correlation	39.69 [59, 60]
XC_GGA_C_XPBE	Extended PBE by Xu & Goddard III	43.85 [63]
XC_GGA_C_LYP	Lee, Yang & Parr	25.88 [101, 102]
XC_GGA_C_P86	Perdew 86	51.36 [103]
XC_GGA_C_PBE_SOL	Perdew, Burke & Ernzerhof correlation SOL	55.32 [75]
XC_GGA_C_PW91	Perdew & Wang 91	51.17 [70, 104]
XC_GGA_C_AM05	Armiento & Mattsson 05 correlation	25.88 [78]
XC_GGA_C_LM	Langreth & Mehl	42.87 [105]
XC_GGA_C_PBE_JRGX	Reparametrized PBE by Pedroza, Silva & Capelle	55.74 [84]
XC_GGA_C_RGE2	Regularized PBE	40.55 [86]
XC_GGA_C_WL	Wilson & Levy	20.95 [106]
XC_GGA_C_WI	Wilson & Ivanov	16.48 [107]
XC_GGA_C_WI0	Wilson & Ivanov initial version	19.42 [107]
XC_GGA_C_APBE	mu fixed from the semiclassical neutral atom	40.86 [95]
XC_GGA_C_SOGGA11	Second-order generalized gradient approximation 2011	40.67 [99]
XC_GGA_C_SOGGA11_X	to be used with XC_HYB_GGA_X_SOGGA11_X	37.05 [108]

GGA Exchange-Correlation

XC_GGA_XC_LB	van Leeuwen & Baerends	29.27 [109]
XC_GGA_XC_HCTH_93	HCTH functional fitted to 93 molecules	155.10 [110]
XC_GGA_XC_HCTH_120	HCTH functional fitted to 120 molecules	151.57 [111]
XC_GGA_XC_HCTH_147	HCTH functional fitted to 147 molecules	143.57 [111]
XC_GGA_XC_HCTH_407	HCTH functional fitted to 147 molecules	155.60 [112]
XC_GGA_XC_EDF1	Empirical functional from Adamson, Gill, and Pople	69.03 [113]
XC_GGA_XC_XLYP	XLYP functional	106.30 [114]
XC_GGA_XC_PBE1W	PBE1W (functional fitted for water)	94.72 [115]
XC_GGA_XC_MPWLYP1W	mPWLYP1w (functional fitted for water)	106.74 [115]

XC_GGA_XC_PBELYP1W	PBELYP1W (functional fitted for water)	79.12	[115]
XC_GGA_XC_KT2	Keal and Tozer, version 2	31.73	[88]
XC_GGA_XC_TH_FL	Tozer and Handy v. FL	94.64	[116]
XC_GGA_XC_TH_FC	Tozer and Handy v. FC	247.35	[116]
XC_GGA_XC_TH_FCFO	Tozer and Handy v. FCFO	372.59	[116]
XC_GGA_XC_TH_FCO	Tozer and Handy v. FCO	355.16	[116]
XC_GGA_XC_TH1	Tozer and Handy v. 1	383.44	[117]
XC_GGA_XC_TH2	Tozer and Handy v. 2	352.52	[118]
XC_GGA_XC_TH3	Tozer and Handy v. 3	332.24	[119]
XC_GGA_XC_TH3	Tozer and Handy v. 4	337.86	[119]

GGA Kinetic Energy

XC_GGA_K_VW	von Weiszaecker correction to Thomas-Fermi	18.49	[120]
XC_GGA_K_GE2	Second-order gradient expansion of the kinetic energy density	16.08	[121, 122]
XC_GGA_K_GOLDEN	TF-lambda-vW form by Golden ($l = 13/45$)	16.39	[123]
XC_GGA_K_YT65	TF-lambda-vW form by Yonei and Tomishima ($l = 1/5$)	13.29	[124]
XC_GGA_K_BALTIN	TF-lambda-vW form by Baltin ($l = 5/9$)	13.24	[125]
XC_GGA_K_LIEB	TF-lambda-vW form by Lieb ($l = 0.185909191$)	14.68	[126]
XC_GGA_K_ABSR1	gamma-TFvW form by Acharya et al [$g = 1 - 1.412/N^{1/3}$]	17.54	[127]
XC_GGA_K_ABSR2	gamma-TFvW form by Acharya et al [$g = 1 - 1.332/N^{1/3}$]	17.01	[127]
XC_GGA_K_GR	gamma-TFvW form by Gázquez and Robles	13.89	[128]
XC_GGA_K_LUDENA	gamma-TFvW form by Ludeňa	18.72	[129]
XC_GGA_K_GP85	gamma-TFvW form by Ghosh and Parr	18.19	[130]
XC_GGA_K_LLP	Becke 88	22.69	[131]
XC_GGA_K_FR_B88	Fuentealba & Reyes (B88 version)	19.97	[92]
XC_GGA_K_FR_PW86	Fuentealba & Reyes (PW86 version)	32.24	[92]
XC_GGA_K_PEARSON	Pearson 1992	13.30	[132, 133]
XC_GGA_K_OL1	Ou-Yang and Levy v.1	20.43	[93]
XC_GGA_K_OL2	Ou-Yang and Levy v.2	20.26	[93]
XC_GGA_K_DK	DePristo and Kress	18.64	[134]
XC_GGA_K_PERDEW	Perdew	16.21	[135]
XC_GGA_K_VSK	Vitos, Skriver, and Kollar	17.05	[136]
XC_GGA_K_VJKS	Vitos, Johansson, Kollar, and Skriver	18.61	[137]
XC_GGA_K_ERNZERHOF	Ernzerhof	18.72	[138]
XC_GGA_K_LC94	Lembarki & Chermette	46.63	[139]
XC_GGA_K_APBE	mu fixed from the semiclassical neutral atom	19.48	[95]
XC_GGA_K_THAKKAR	Thakkar 1992	24.92	[140]
XC_GGA_K_TW1	Tran and Wesolowski set 1 (Table II)	18.70	[141]
XC_GGA_K_TW2	Tran and Wesolowski set 2 (Table II)	18.30	[141]
XC_GGA_K_TW3	Tran and Wesolowski set 3 (Table II)	19.01	[141]
XC_GGA_K_TW4	Tran and Wesolowski set 4 (Table II)	19.97	[141]

MetaGGA Functionals

MetaGGA Exchange

XC_MGGA_X_LTA	Local tau approximation	24.07	[142]
XC_MGGA_X_TPSS	Perdew, Tao, Staroverov & Scuseria exchange	28.88	[143, 144]
XC_MGGA_X_TAU_HCTH,	Tau HCTH	23.45	[145]
XC_MGGA_X_GVT4	GVT4 (exchange part of VSXC)	26.85	[146]
XC_MGGA_X_M06L	M06-L	29.74	[147, 148]
XC_MGGA_X_BR89	Becke-Roussel 89	49.39	[149]
XC_MGGA_X_BJ06	Becke & Johnson 06	35.28	[150]
XC_MGGA_X_TB09	Tran & Blaha 09	31.96	[151]

XC_MGGA_X_RPP09	Rasanen, Pittalis & Proetto 09	44.16	[152]
XC_MGGA_X_2D_PRHG07	Pittalis-Rasanen-Helbig-Gross 2007	54.18	[153]
XC_MGGA_X_2D_PRHG07_PRP10	Corrected Pittalis-Rasanen-Helbig-Gross 2010	53.94	[153]

MetaGGA Correlation

XC_MGGA_C_TPSS	Perdew, Tao, Staroverov & Scuseria correlation	184.60	[143, 144]
XC_MGGA_C_VSXC	VSXC (correlation part)	148.84	[146]

Hybrid Functionals

Hybrid Exchange

XC_HYB_GGA_X_SOGGA11_X	Hybrid based on SOGGA11 form (see also XC_GGA_C_SOGGA11_X)	21.13	[108]

Hybrid Exchange-Correlation

XC_HYB_GGA_XC_B3PW91	The original hybrid proposed by Becke	99.90	[154]
XC_HYB_GGA_XC_B3LYP	The (in)famous B3LYP	93.55	[155]
XC_HYB_GGA_XC_B3P86	Perdew 86 hybrid similar to B3PW91	105.17	
XC_HYB_GGA_XC_O3LYP	hybrid using the optx functional	78.60	[156]
XC_HYB_GGA_XC_PBEH	PBEH, also known as PBE0	76.12	[157]
XC_HYB_GGA_XC_X3LYP	X3LYP	120.61	[114]
XC_HYB_GGA_XC_B1WC	B1WC	78.94	[158]
XC_HYB_GGA_XC_B97	Becke 97	158.49	[65]
XC_HYB_GGA_XC_B97_1	Becke 97-1	154.97	[110]
XC_HYB_GGA_XC_B97_2	Becke 97-2	151.12	[159]
XC_HYB_GGA_XC_B97_K	Becke 97-K, Boese-Martin for Kinetics	158.38	[160]
XC_HYB_GGA_XC_B97_3	Becke 97-3	155.92	[161]
XC_HYB_GGA_XC_B1LYP	B1LYP	52.18	[162]
XC_HYB_GGA_XC_B1PW91	B1PW91	69.92	[162]
XC_HYB_GGA_XC_mPW1PW	mPW1PW	99.96	[81]
XC_HYB_GGA_XC_mPW3PW	mPW3PW of Adamo & Barone	110.82	[81]
XC_HYB_GGA_XC_mPW3LYP	mPW3LYP	112.92	[163]
XC_HYB_GGA_XC_SB98_1a	SB98 (1a)	149.81	[164]
XC_HYB_GGA_XC_SB98_1b	SB98 (1b)	156.87	[164]
XC_HYB_GGA_XC_SB98_1c	SB98 (1c)	158.72	[164]
XC_HYB_GGA_XC_SB98_2a	SB98 (2a)	139.63	[164]
XC_HYB_GGA_XC_SB98_2b	SB98 (2b)	148.48	[164]
XC_HYB_GGA_XC_SB98_2c	SB98 (2c)	158.78	[164]
XC_HYB_GGA_XC_mPW1K	mPW1K	100.53	[165]

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